On Tropospheric Tracer Correlations: Ethane & Propane

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Stratospheric tracer correlations

Plumb & Ko (1992): Slope equilibrium for long-lived tracers

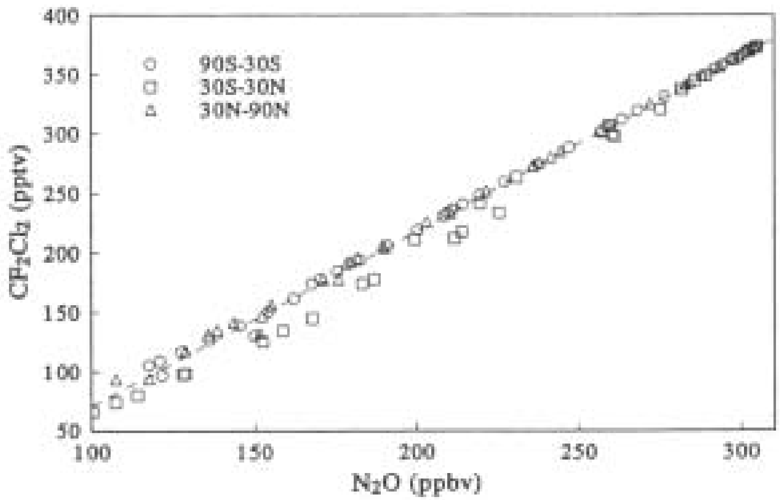


Fig. 5. Correlation diagram for January between CF_2Cl_2 and N_2O from the 2D model. In the upper panel, monthly mean values from all grid boxes are shown. Lower panel shows all model points with $\sigma[N_2O]>100$ ppbv; the dashed line is the least squares straight line fit to the points and is defined by $\sigma[F11] = 0.00147\ \sigma[N_2O] - 0.0763$ ppbv. Points are labeled according to latitude.

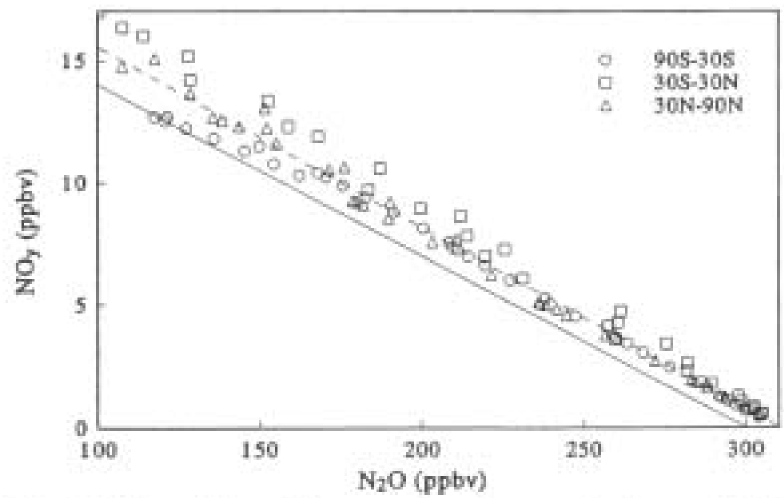


Fig. 6. Correlation diagram for January between total reactive nitrogen NO_y and N_2O from the 2D model. Upper panel shows data over the full range; lower panel for the subrange $\sigma[N_2O]>$ 100 ppbv. The dashed line represents the least squares fit to the model points shown in the lower panel; the slope of the solid line is that determined from lower stratospheric observations by Fahey et al. [1990].

2-D simulations; horizontal mixing time scale << chemical lifetimes

Stratospheric tracer correlations

Avollone & Prather (1997): AASE II & 3-D model simulations

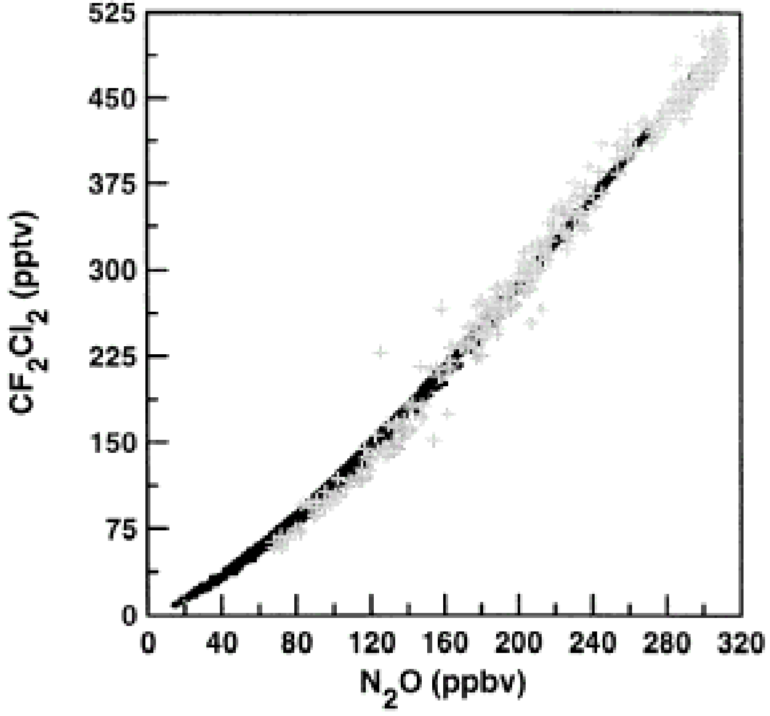


Figure 2. Scatterplot of CF_2Cl_2 (CFC-12) versus N_2O (nitrous oxide). Small black dots are points from CTM calculation. The gray pluses are *in situ* observations from AASE II made by the NCAR and UCI whole air samplers.

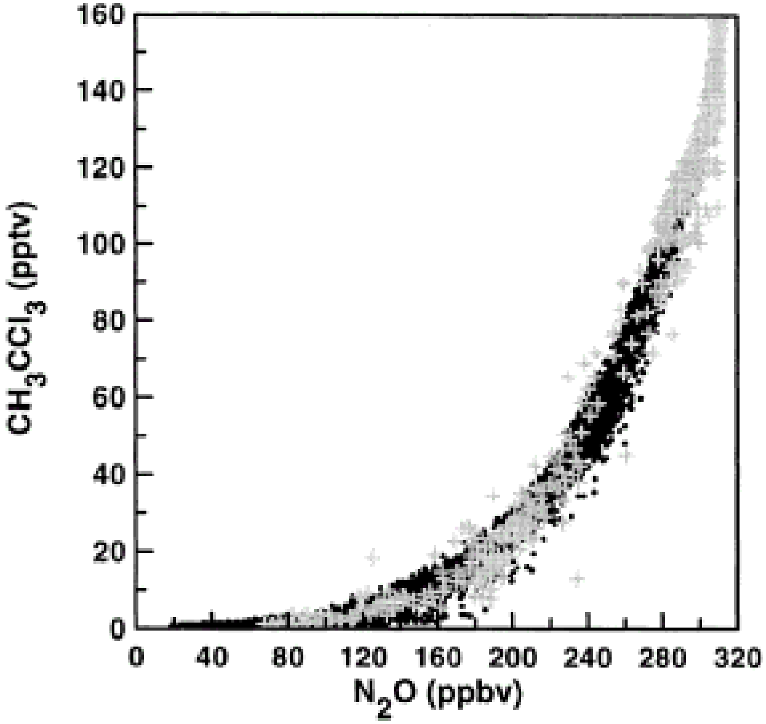


Figure 7. Same as Figure 2 but for CH_3CCl_3 (methyl chloroform).

CFC-12 lifetime ~ 4x CH_3CCl_3

Tropospheric tracer correlations

Kinetics slope and mixing

- There is usually a good correlation between two light NMHCs in the log space (not the linear space of PK92)
- Tracer concentrations and the ratio of two tracers respond differently to mixing (Parrish et al., 1992)
- The correlation is determined by the interplay of chemistry and mixing (McKeen & Liu, 1993; McKeen et al., 1996).

Tropospheric tracer correlations

McKeen & Liu (1993): Simple mixing model

$$\frac{dX}{dt} = -l^c X - l^m (X - X^b)$$

- The correlation is bounded by the kinetics and mixing lines
- The mixing rate constant, l^m, has to be determined with 3-D model simulations (where oxidation rates can be calculated).
- The background mixing ratio, X^b, must be specified
- The correlation in log space is not linear when X approaches X^b (unless $X^b = 0$)

Tropospheric tracer correlations

Ethane and propane

Observations

- TOPSE
- TRACE-P
- PEM-Tropics A
- PEM-Tropics B

The correlation is much better in TOPSE and PEM-Tropics B than TRACE-P and PEM-Tropics A (when fresh emission were sampled)

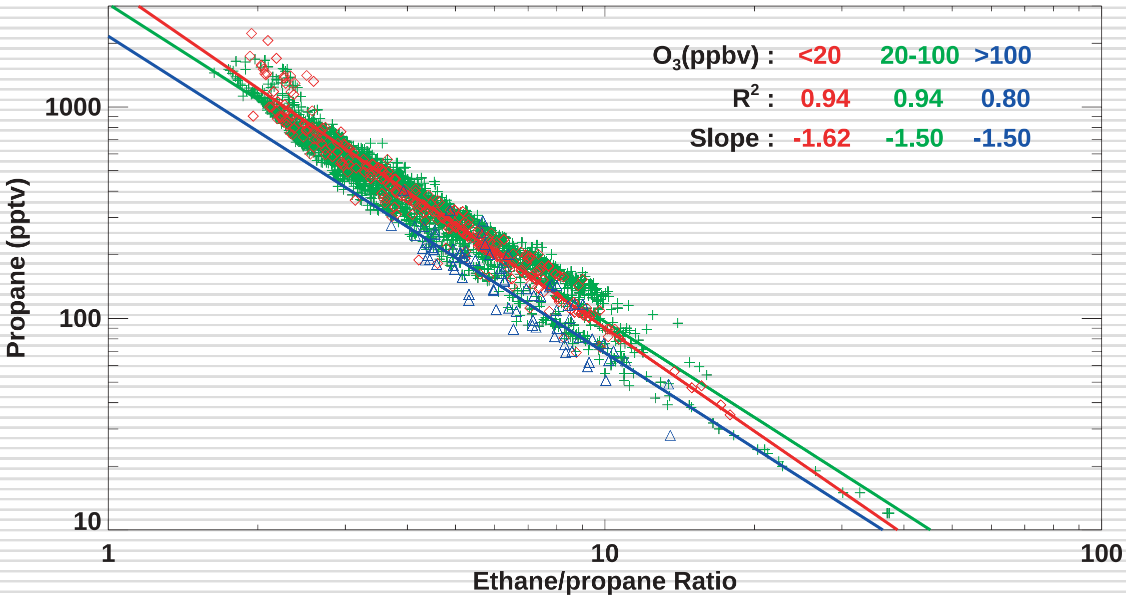
GEOS-CHEM

(Bey et al., 2001)

- 4°x5°, 26 vertical layers in the trop
- GMAO GEOS-3 2000 year meteorology
- Model spin-up time: 1 year
- Hourly data output

Tropospheric tracer correlations

Northern mid and high latitudes (TOPSE)



The correlations between propane and ethane/propane ratio during TOPSE. Three data groups for O_3 mixing ratios of < 20 (halogen chemistry), 20-100, and > 100 ppbv (stratosphere influenced) are shown.

We chose the examine the correlation between propane and ethane/propane ratios rather than that between ethane and propane because (1) the former is more invariant to temperature and (2) propane and ethane/propane ratio respond to mixing differently (Parrish et al., 1992).

Tropospheric tracer correlations
“Finite mixing” model

- Kinetics slope of the correlation of propane and ethane/propane ratio (1.24±0.07)

$$|\beta|^c = \frac{k_2}{k_2 - k_1}$$

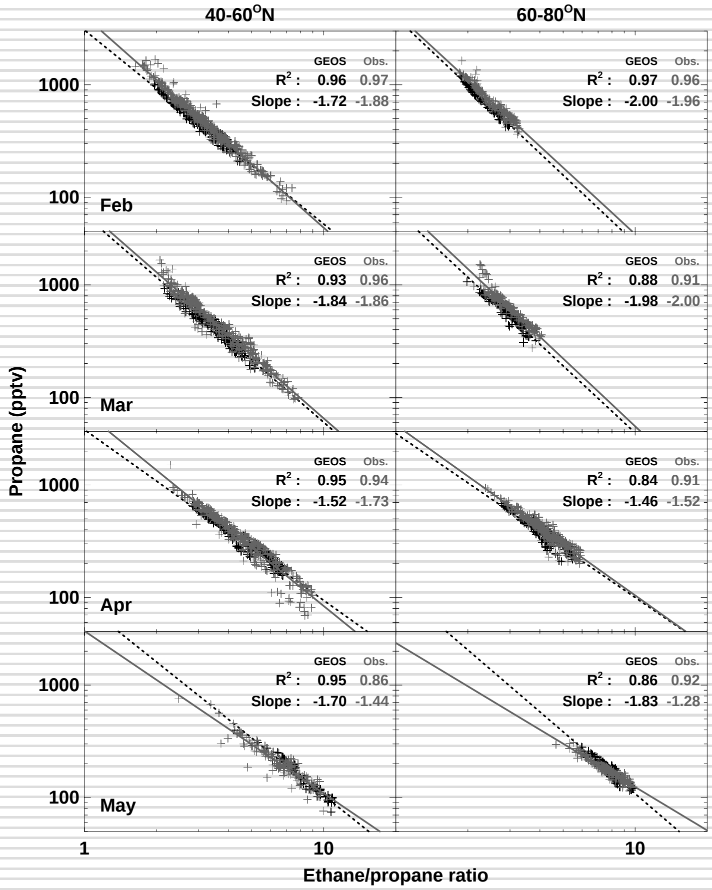
(1 for ethane, 2 for propane)

- “Finite mixing” model

$$|\beta| = \frac{k_2}{k_2 - k_1 + (1 - \lambda_1/\lambda_2)k_1} \approx |\beta|^c \left(1 + \frac{(\lambda_1/\lambda_2 - 1)k_1}{k_2 - k_1}\right)$$

- λ is the augmentation factor of mixing relative to photochemistry. $\lambda_{ethane} > \lambda_{propane}$ because chemical oxidation of propane is much faster than ethane. Hence $|\beta| > |\beta|^c$

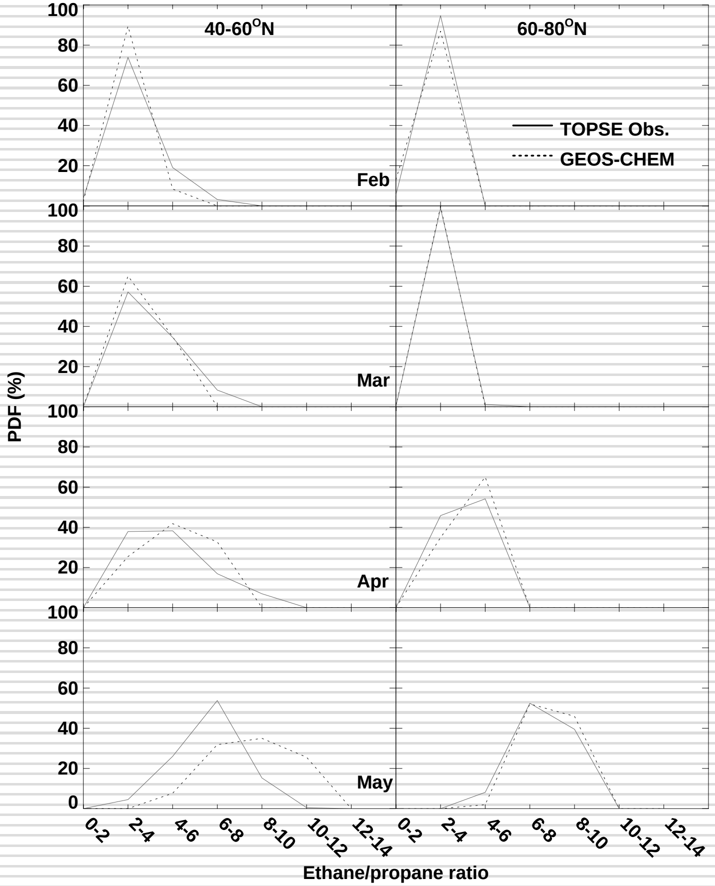
Northern mid and high latitudes (TOPSE) Seasonal change of the correlation



- $|\beta| > |\beta|^c$
- Observed $|\beta|$ approaches the kinetics slope as photochemistry becomes more important
- Simulated slopes show a different transition from April to May
- Mixing effect is overestimated relative to chemistry effect, particularly in May

Observed and simulated correlations between propane and ethane/propane ratio for data with ethane/propane ratios in the lower 90th percentile as a function of latitude and month. The selected observation data have O3 mixing ratios between 20 and 100 ppbv.

Northern mid and high latitudes (TOPSE) Seasonal change of the PDF

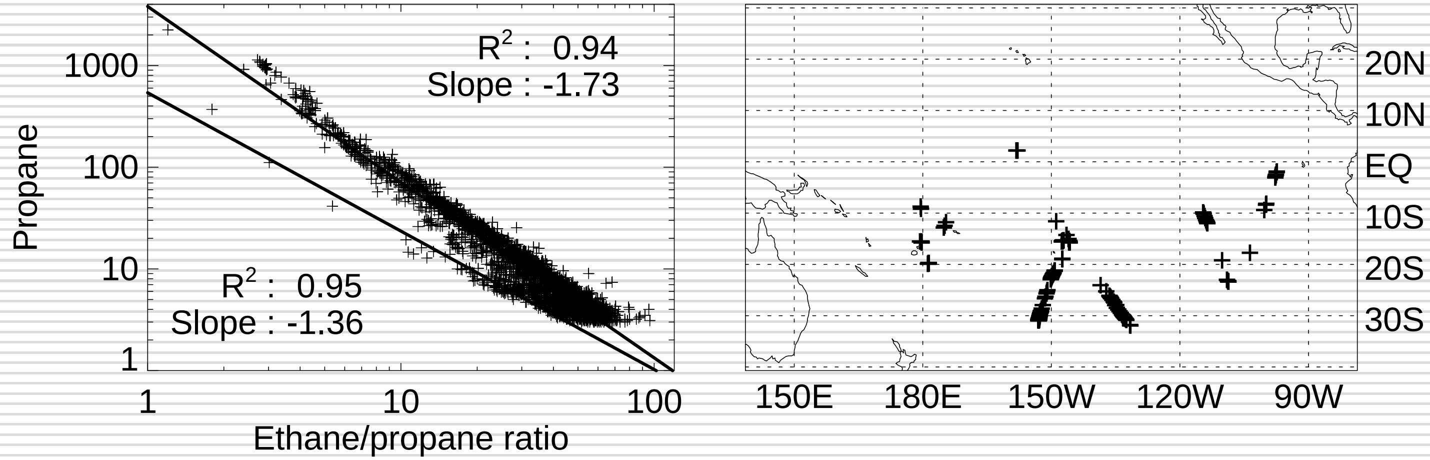


- The seasonal shift of PDF towards higher ethane/propane ratios is well simulated
- The high bias at mid latitudes in May reflect excessive transport of high ethane/propane ratio air from lower latitudes
- No evidence for underestimating chemical oxidation
- Mixing in the model is therefore overestimated in May resulting in the large overestimates of $|\beta|$ values in the correlation.

Observed and simulated probability distribution functions (PDFs) of ethane/propane ratios in the lower 90th percentile at mid and high latitudes from February to May during TOPSE.

Tropical Pacific (PEM-Tropics B)

Two-branch structure: observations

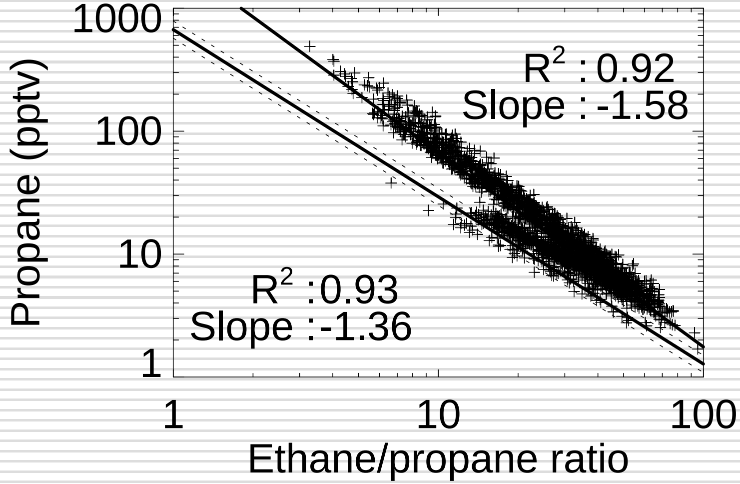


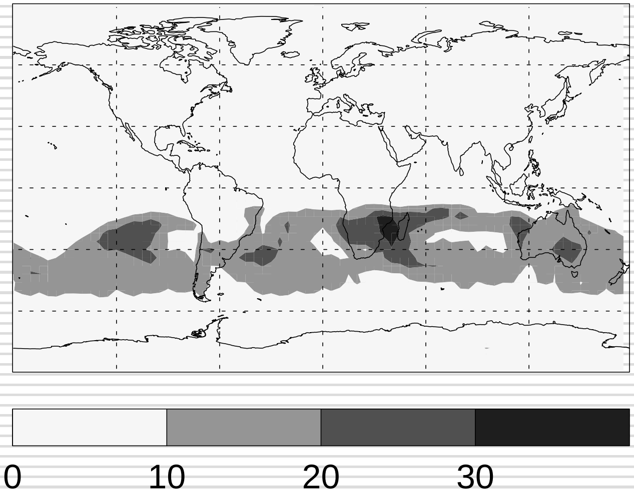
- The major correlation slope is similar to those from TOPSE in March and April reflecting the effect of ethane and propane transported from the northern hemisphere
- The minor correlation slope is closer to the kinetics slope

Observed correlation between propane and ethane/propane ratio during PEM-Tropics B. The right panel shows the locations of data points for the minor correlation branch

Tropical Pacific (PEM-Tropics B)

Two-branch structure: simulation





- The two-branch structure is simulated in the model
- The slope of the major correlation is less than observed (in magnitude)
- The minor branch data points reside in the southern mid latitudes

Simulated correlation between propane and ethane/propane ratio for PEM-Tropics B. The first of 50 synthetic data sets is shown. The right panel shows the percentages of data that fall into the region bounded by the dashed lines (± 1 standard deviation around the minor correlation line) in the left panel.

Tropical Pacific (PEM-Tropics B)
Effects of convection

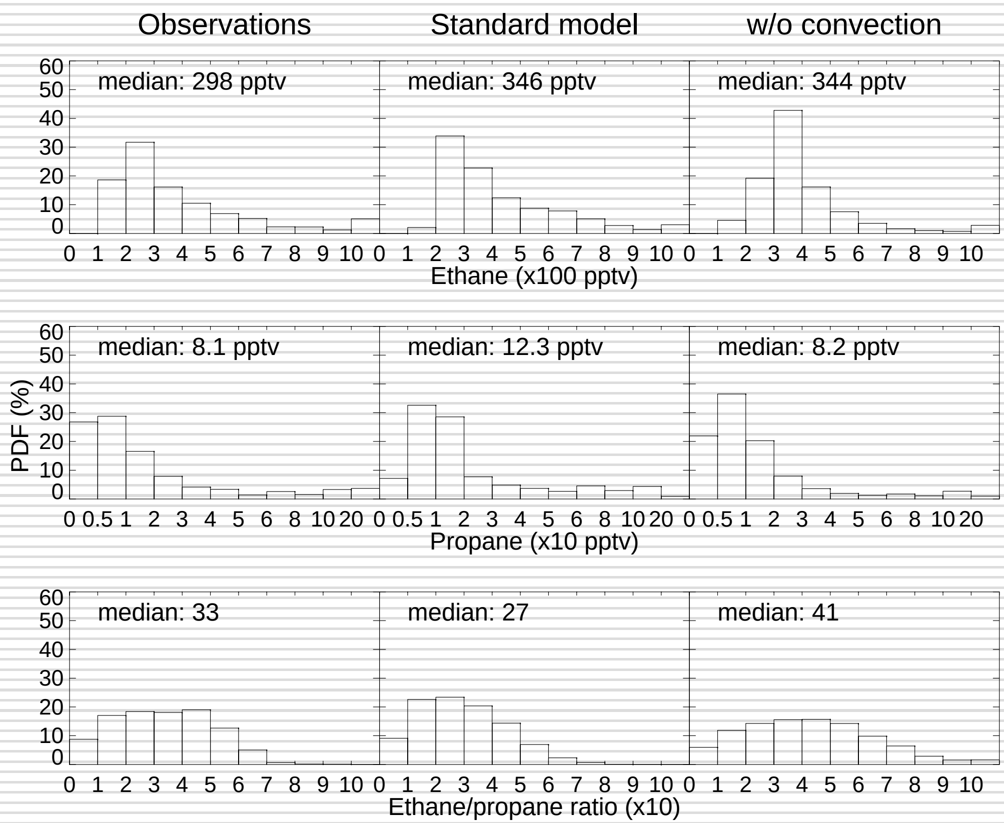
Table 1. The absolute slopes of the correlations between propane and ethane/propane ratio for each source category in the standard "tagged tracer" simulation and that without convection.

Sources	Standard simulation	No convection
All (major correlation)	1.58	1.43
Biomass	1.53	1.46
Biofuel	1.63	1.51
Industry (N. America)	1.65	1.54
Industry (S. America)	1.40	1.36
Industry (Europe)	1.67	1.52
Industry (N. Africa)	1.48	1.44
Industry (S. Africa)	1.36	1.34
Industry (N. Asia)	1.64	1.46
Industry (S. Asia)	1.50	1.43
Industry (Australia)	1.45	1.38

- In the standard simulation, the slopes for emissions from the southern hemisphere are less than those for northern industrial sources
- Without convection, the slopes decrease in magnitude because mixing is suppressed
- The decrease of slope magnitude without convection is most significant for northern industrial sources

Tropical Pacific (PEM-Tropics B)

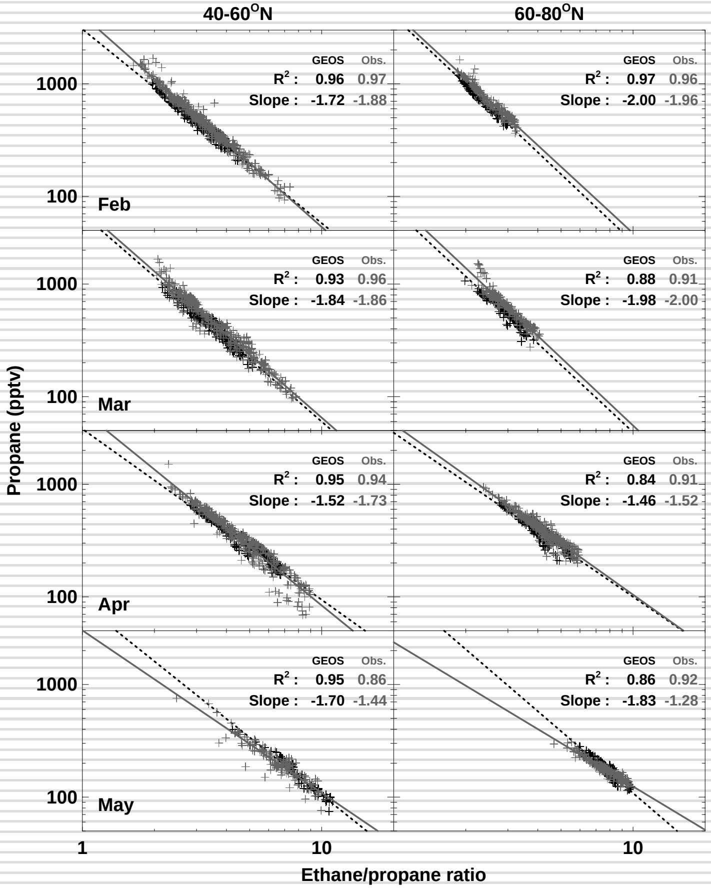
PDF distributions



- There is no evidence that photochemical oxidation is overestimated in the model
- Therefore the underestimate of the major correlation slope implies that convection at northern industrial regions is underestimated
- Transport from northern industrial regions to the tropics is overestimated resulting in the failure of simulating population with low ethane and propane

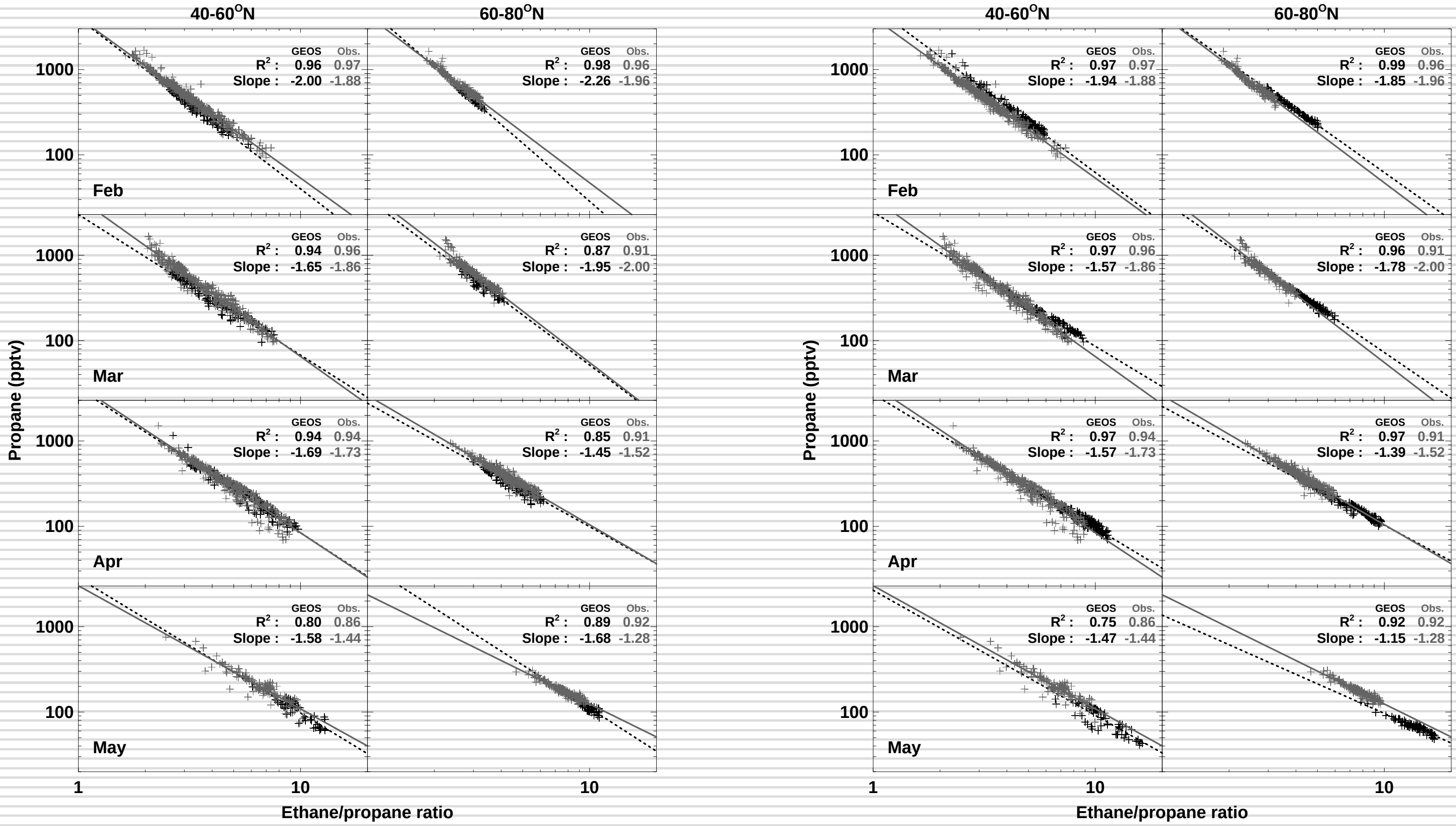
Observed and simulated PDFs of ethane, propane, and ethane/propane ratio. Results from the standard model and the one without convection are shown.

Tropospheric tracer correlations
Implication for inverse modeling



- Systematic transport bias will lead to bias in the inverse modeling
- Based on our evaluation of model simulations for TOPSE and PEM-Tropics B, the model did not show systematic biases only in March at mid latitudes and February-April at high latitudes
- With the subset of data, we estimate that the emissions are underestimated by 14±5%

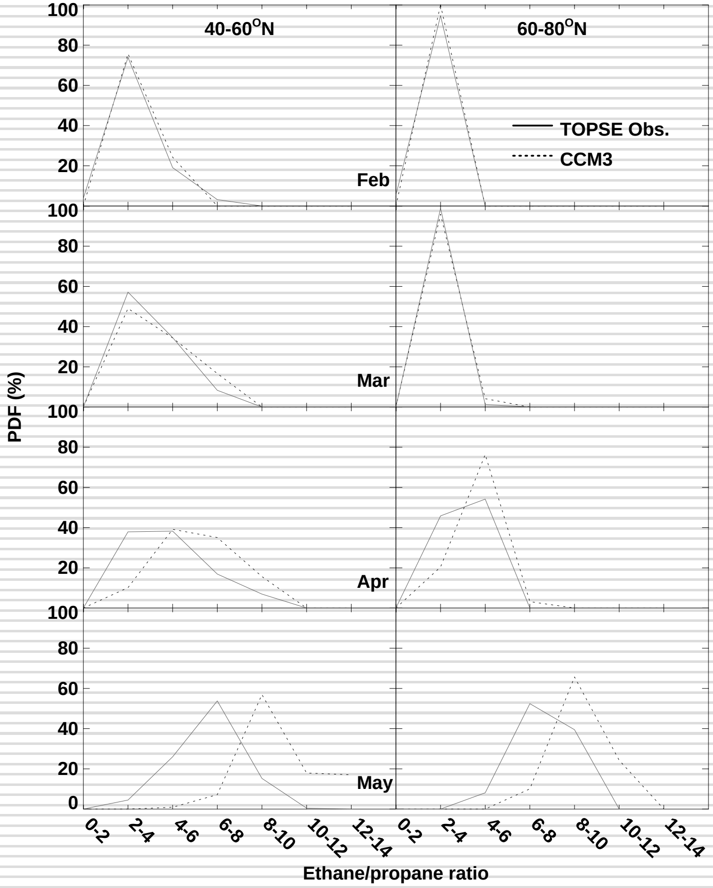
GMI
TOPSE: Different slope trends



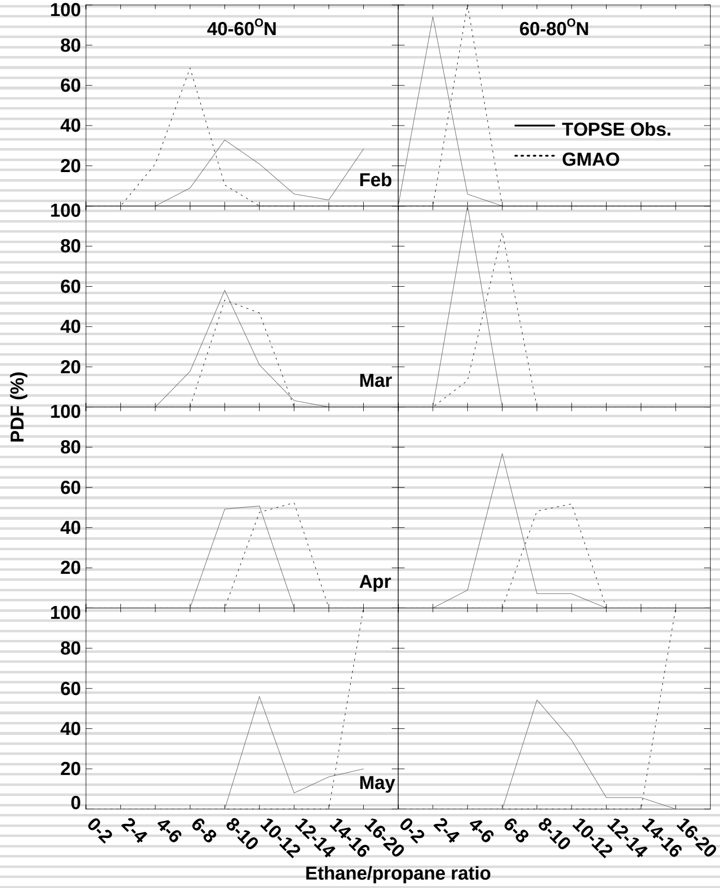
CCM3 GEOS-Strat

GMI

TOPSE: Overestimate of ethane/propane ratios

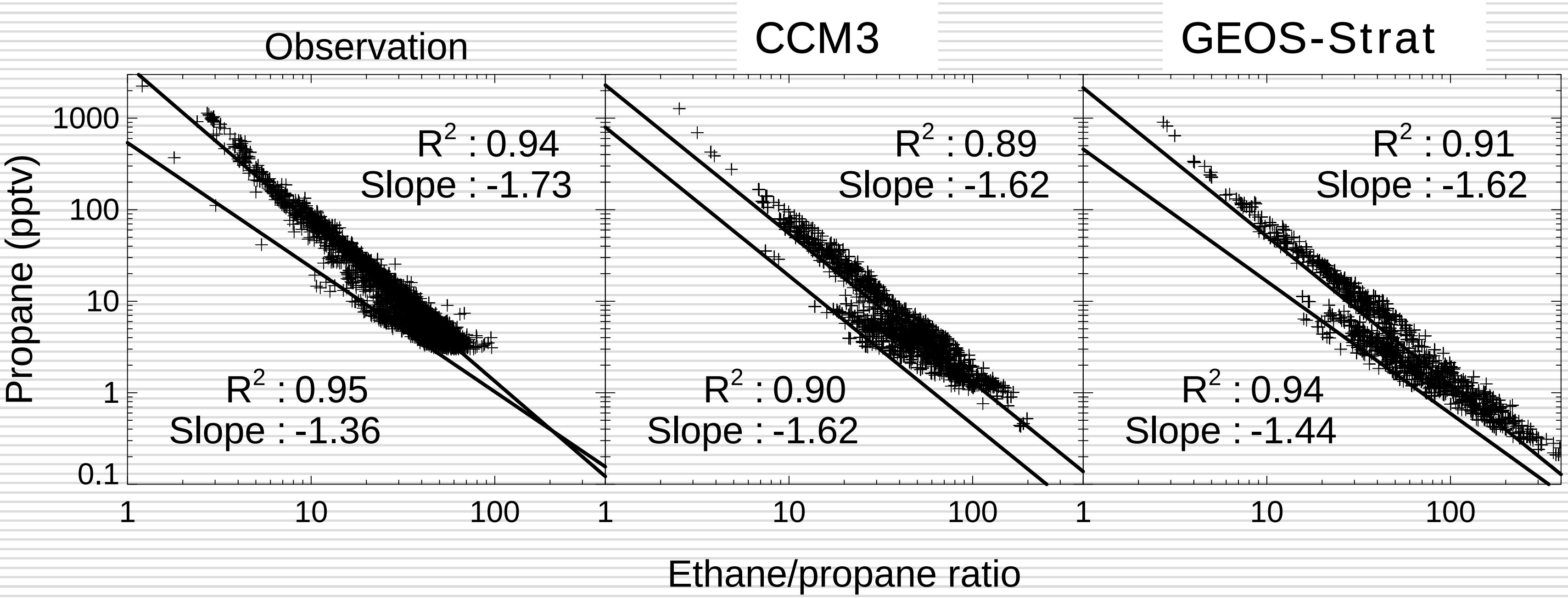


CCM3



GEOS-Strat

GMI
PEM-Tropics B



GMI

PEM-Tropics B: Too much OH?